EXHIBIT A

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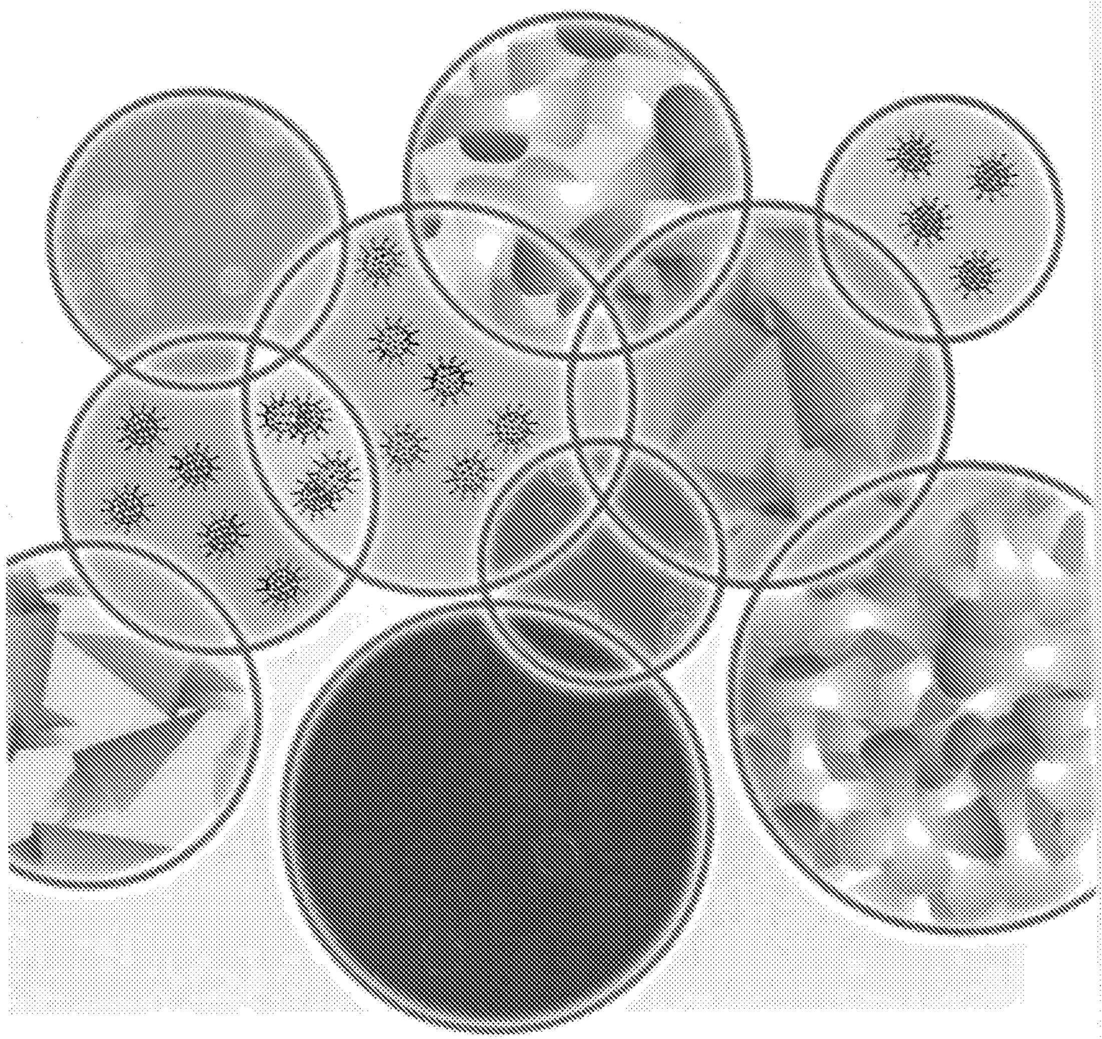

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1.7
Selection of Emulsifiers

1.7.1
The Hydrophilic-Lipophilic Balance (HLB) Concept

Today, the selection of different surfactants in the preparation of either O/W or W/O emulsions is often made on an empirical basis. One such semi-empirical scale for selecting surfactants is the hydrophilic-lipophilic balance (HLB) number developed by Griffin [18]. This scale is based on the relative percentage of hydrophilic to lipophilic (hydrophobic) groups in the surfactant molecule(s). For an O/W emulsion droplet the hydrophobic chain resides in the oil phase, while the hydrophilic head group resides in the aqueous phase. In contrast, for a W/O emulsion droplet the hydrophilic group(s) reside in the water droplet, whereas the lipophilic groups reside in the hydrocarbon phase.

A guide to the selection of surfactants for particular applications is provided in Table 1.2. Here, the HLB number is seen to depend on the nature of the oil and, as an illustration, the required HLB numbers to emulsify various oils are listed in Table 1.3.

The relative importance of the hydrophilic and lipophilic groups was first recognized when using mixtures of surfactants containing varying proportions of low and high HLB numbers. The efficiency of any combination (as judged by phase separation) was found to pass a maximum when the blend contained a particular proportion of the surfactant with the higher HLB number. This is illustrated in Figure 1.23, which shows the variation of emulsion stability, droplet size and interfacial tension in relation to the percentage of surfactant with a high HLB number.

Table 1.2 A summary of surfactant HLB ranges and their applications.

HLB range	Application
3–6	W/O emulsifier
7–9	Wetting agent
8–18	O/W emulsifier
13–15	Detergent
15–18	Solubilizer

Table 1.3 HLB numbers required for the emulsification of various oils.

Oil	W/O emulsion	O/W emulsion
Paraffin oil	4	10
Beeswax	5	9
Linolin, anhydrous	8	12
Cyclohexane	–	15
Toluene	–	15

The average HLB number may be calculated from additivity:

$$\mathrm{HLB} = x_1 \mathrm{HLB}_1 + x_2 \mathrm{HLB}_2 \tag{1.48}$$

where x_1 and x_2 are the weight fractions of the two surfactants with HLB_1 and HLB_2, respectively.

Griffin developed simple equations for calculating the HLB number of relatively simple nonionic surfactants. For example, in the case of a polyhydroxy fatty acid ester

$$\mathrm{HLB} = 20\left(1 - \frac{S}{A}\right) \tag{1.49}$$

where S is the saponification number of the ester and A is the acid number. For a glyceryl monostearate, $S = 161$ and $A = 198$, and the HLB is 3.8 (suitable for W/O emulsion).

For a simple alcohol ethoxylate, the HLB number can be calculated from the weight percent of ethylene oxide (E) and polyhydric alcohol (P):

$$\mathrm{HLB} = \frac{E + P}{5} \tag{1.50}$$

If the surfactant contains PEO as the only hydrophilic group, then the contribution from one OH group may be neglected:

$$\mathrm{HLB} = \frac{E}{5} \tag{1.51}$$

For a nonionic surfactant $C_{12}H_{25}{-}O{-}(CH_2{-}CH_2{-}O)_6$, the HLB is 12 (suitable for O/W emulsion).

The above simple equations cannot be used for surfactants containing propylene oxide or butylene oxide; neither can they be applied for ionic surfactants. Davies [19, 20] devised a method for calculating the HLB number for surfactants from their chemical formulae, using empirically determined group numbers. A group number is assigned to various component groups (a summary of the group numbers for some surfactants is shown in Table 1.4).

The HLB is then given by the following empirical equation:

$$\mathrm{HLB} = 7 + \Sigma(\text{hydrophilic group Nos}) - \Sigma(\text{lipophilic group Nos}) \tag{1.52}$$

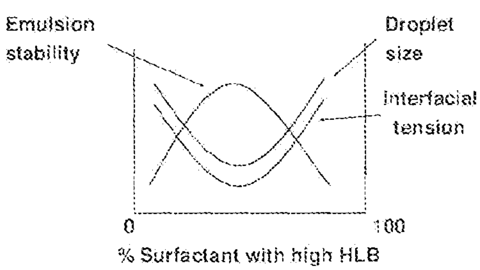

Figure 1.23 Variation of emulsion stability, droplet size and interfacial tension in relation to the percentage of surfactant with a high hydrophilic–lipophilic balance (HLB) number.

Table 1.4 HLB group numbers.

Surfactant type/group	Group number
Hydrophilic	
$-SO_4Na^+$	38.7
$-COO^-$	21.2
$-COONa$	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
$-O-$	1.3
CH–(sorbitan ring)	0.5
Lipophilic	
$(-CH-)$, $(-CH_2-)$, CH_3	0.475
Derived	
$-CH_2-CH_2-O$	0.33
$-CH_2-CH_2-CH_2-O-$	−0.15

Davies has shown that the agreement between HLB numbers calculated from the above-described equation and those determined experimentally is quite satisfactory.

Various other procedures have been developed to obtain a rough estimate of the HLB number. Griffin found a good correlation between the cloud points of 5% solutions of various ethoxylated surfactants and their HLB numbers.

Davies [19, 20] also attempted to relate the HLB values to the selective coalescence rates of emulsions. These correlations were not realized as the emulsion stability and even its type were found to depend to a large extent on the method of dispersing the oil into the water, and *vice versa*. At best, the HLB number can only be used as a guide for selecting the optimum compositions of emulsifying agents.

It is possible to take any pair of emulsifying agents, which fall at opposite ends of the HLB scale, for example Tween 80 (sorbitan mono-oleate with 20 moles EO, HLB = 15) and Span 80 (sorbitan mono-oleate, HLB = 5) and to use them in various proportions to cover a wide range of HLB numbers. The emulsions should be prepared in the same way, with a few percent of the emulsifying blend. The stability of the emulsions is then assessed at each HLB number, either from the rate of coalescence, or qualitatively by measuring the rate of oil separation. In this way it is possible to determine the optimum HLB number for a given oil. Having found the most effective HLB value, various other surfactant pairs are compared at this HLB value, to identify the most effective pair.

1.7.2
The Phase Inversion Temperature (PIT) Concept

Shinoda and coworkers [21, 22] found that many O/W emulsions, when stabilized with nonionic surfactants, undergo a process of inversion at a critical temperature (known as the PIT). The PIT can be determined by following the emulsion conduc-